AD-A184 958

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Final Report ARO 21367.6-CH	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Activated Metal Oxide Surfaces as Highly Basic and Reducing Environments		5. TYPE OF REPORT & PERIOD COVERED Final Report 4/84-3/87
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Kenneth J. Klabunde		8. CONTRACT OR GRANT NUMBER(s) DAAG29-84-K-0051
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Kansas State University Manhattan, Kansas 66506		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE May, 1987
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

DTIC
ELECTE
SEP 1 7 1987
E

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Metal oxide, super base, thermal activation, defect sites

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Alkaline earth oxides of high surface area were thermally activated at 400-1100°C. Super base properties and electron transfer sites were generated. These materials serve as catalysts for selective deuteration of hydrocarbons, alkene isomerization, CO telomerization and reduction, carbonyl compound condensation, and as a destructive adsorbent for organophosphorus compounds and other toxic substances. Some fundamental understanding of the reactive sites involved has been gained by studying adsorbed species and by metal ion doping. Studies of single metal oxide molecules in matrices has begun.

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE

8

Activated Metal Oxide Surfaces as
Highly Basic and Reducing Environments

Final Report

Kenneth J. Klabunde

May 21, 1987

U.S. Army Research Office

DAAG29-84-K-0051

Kansas State University
Department of Chemistry
Manhattan, KS 66506

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

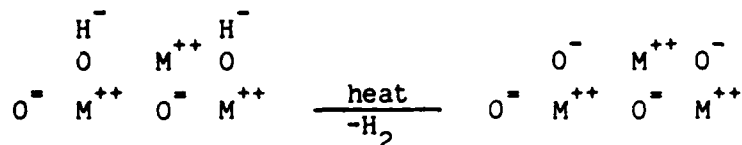Approved for public release; distribution unlimited

I. Introduction

Although metal oxides play an important technological role in the chemical industry (polymer additives, food additives, catalyst supports and promotors, chromatography, paints, etc.), the rich surface chemistry of metal oxides has only recently begun to be appreciated. This is especially true of the alkaline earth oxides which are capable of exhibiting "super base" and "super reducing" abilities.[1] The key to further understanding of this rich area of chemistry is to appreciate that surface defects are generally the reactive sites, and that the defects generated are very dependent on preparative method and activation procedure.

The physics community has done a considerable amount of work trying to outline the multitude of defects that can occur on alkaline earth oxide surfaces.[2,3] However, presumably due to their complexity, the chemistry community has dealt with the subject sparingly. Admittedly, these are very difficult systems to understand. However, the potential technological payoff now dictates that these studies be undertaken more seriously. (The Japanese and French scientific communities have been most active in metal oxide surface work, especially as it relates to catalysis.)[4,5]

Unique Physical Properties of Metal Oxides:

(1) The high heats of formation of the insulator oxides (eg MgO, CaO, SiO_2, and Al_2O_3) and their ionic character allow them to form high surface area,[6] nearly amorphous states with very good thermal stabilities. Reactive defect sites are often formed in high concentrations during preparation.

(2) The defect sites[2,3,7] are of several types: (a) steps and kinks on surfaces;[8] (b) ion vacancies called Frenkel or Schottky defects;[9] and (c) paramagnetic defects called F or V centers formed by electron capture or loss from ion vacancies.[8,10] A myriad of variations are possible depending on the surrounding geometrical and electronic environment around the defect in question, and whether OH groups exist on the surface.[3,6]

(3) Cation size and M:O stoichiometry can cause unusual crystallite structures to be formed. For Example BeO has the Wurtzite structure (hexagonal close packed arrangements of O^-) while MgO, CaO, SrO, and BaO adopt the rock salt structure. Al_2O_3 can have different phases; the β-structure possesses tunnels which allow ionic conductive properties when doped with Li^+ or Na^+.[6]

(4) Metal oxide surfaces can be activated by irradiation, which dislodges electrons which are captured at defect sites, or by heating under vacuum or under a rapid flow of N_2 or Ar to a specified temperature in the range of 400-1200°C.[21] Heating causes structural defects to form, and to become available through a cleaning process. Thus, H_2O, CO_2 and other adsorbed species are removed. In addition, chemical processes such as H_2 elimination from surface OH groups can lead to additional reactive sites such as electron deficient centers:

$$
\begin{array}{ccccc}
\overset{H^-}{O} & M^{++} & \overset{H^-}{O} & & O^- \quad M^{++} \quad O^- \\
O^{\bullet} \quad M^{++} \quad O^{\bullet} \quad M^{++} & \xrightarrow[-H_2]{\text{heat}} & O^{\bullet} \quad M^{++} \quad O^{\bullet} \quad M^{++}
\end{array}
$$

(5) Activation temperature and doping with other ionic metal oxides can have a dramatic effect on chemical reactivities.

Unique Chemical Properties of Metal Oxides:

(1) Super base properties can be generated.[12]

(2) Super acid (eg. ZrO_2 - Na_2SO_4) properties can be generated.[13,14]

(3) Activated MgO is basic enough that it can be used conveniently as a deuteration catalyst for hydrocarbons such as methane by the reaction $CH_4 + D_2 \rightarrow CH_3D + HD$.[15]

* (4) MgO can also be used for selective deuteration of toluene, ethylbenzene, and other hydrocarbons.[16]

* (5) Relative acidities of hydrocarbons such as toluene, xylene, and even neopentane can be determined using activated MgO as a deuterium exchange catalyst.[17]

* (6) Acidity determinations over MgO parallel solution acidities rather than gas phase acidities.[17,18]

* (7) H-D exchange from $H_2 + D_2$ and RH(benzylic) + D_2 have extremely low Ea (~1-2 kcal/mole)[16,29] which indicates a strong bifunctional catalytic mechanism where both M^{++} and $O^{\bullet}$ are involved simultaneously.

(8) Activated MgO can be used as a hydrogenation catalyst for organic dienes. When D_2 is used, no H-D scrambling occurs if the MgO activation is carried out at 1100°C. Thus, catalytic sites for D_2 addition or H-D exchange are different, and one or the other can be favored by activation procedure.[20]

(9) Methane can be partially converted to ethane in a slightly oxidizing environment over MgO.[21] Activity can be enhanced by Li^+ doping.

* (10) Doping of MgO with Li^+, Na^+, and Al^{3+} can have dramatic effects on catalytic reaction rates for 1-butene isomerization vs electron transfer to CO to form $(CO)_6^{3-}$.[22]

* (11) Chemisorption processes on activated MgO often involve electron transfer from defect sites to the adsorbed molecule. Thus, nitrobenzene, benzophenone, napthalene, anthracene, and others chemisorb at room temperature to form monolayers of anion-radicals.[23,24]

* (12) Chemisorption of CO at 25°C causes both telomerization and electron transfer, yielding a variety of $(CO)_n^{x-}$ species, particularly $(CO)_6^{2-}$ and $(CO)_6^{3-}$.[24]

* (13) Organic carbonyl compounds are strongly chemisorbed and base induced condensation reactions readily carried out over activated MgO,[25]

* (14) Activated MgO is an extremely effective material, due to its high surface area and high concentration of very basic defect sites, for adsorption and destruction of organophosphorous compounds, and it shows promise as a sorbent for air purification systems.[26]

II. Summary of Work Completed Under the Past ARO Contract (3/84-3/87)

A. Unique Chemical Properties of Activated MgO

In the Introduction a list of Unique Chemical Properties is given. Those marked with an asterisk are areas we have contributed to (see pages 6-7).

B. Structural Aspects Regarding Reactive Sites

When dealing with the complexities of metal oxide surfaces and the knowledge that a variety of reactive defect sites are possibly important, the major problem becomes one of understanding chemical reactivity on the molecular level. Here we outline some of our recent investigations aimed at improving our current understanding at this level.

1. Doping with Li^+, Na^+, and Al^{3+}

To encourage the formation of Frenkel and Schottky defects as well as electron deficient/excess centers, MgO was doped with Li^+, Na^+, and Al^{3+} as their oxides. Chemical probes CO → $(CO)_6^{3-}$ and 1-butene isomerization have been employed, and suggested that electron rich and electron deficient substructures were formed, as illustrated by $[Mg_9Li_3O_{12}]^{3-}$ and $[Mg_9Al_3O_{12}]^{3+}$. Unique reaction properties were described.[22]

2. Spin Traps

Organic nitroso and nitrone compounds are capable of trapping transient free radicals (R·) or free electrons to form stable, paramagnetic adducts that exhibit ESR spectra characteristic of R· (or e-) trapped.[27] In addition, nitroxide radicals adsorbed on surfaces can yield information about adsorption sites.

Since activated MgO can possess paramagnetic defect sites (that are difficult to detect by ESR due to relaxation times), and electron transfer sites, we carried out a study of species formed upon adsorption of NOMP and PNP on its surface. We made the following observations:[28] depending on

$$(CH_3)_3C-N=O$$
NOMP

$$C_6H_5CH-N^+-C_6H_5$$
PNP

(with O⁻ above the N)
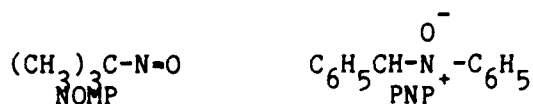
activation temperature three species were formed NOMP·-o-surface (trapped surface O⁻), PNP⁻ or NOMP⁻ (electron donated to NOMP or PNP), and di-t-butynitroxide (decomposition of NOMP and subsequent trapping of $(CH_3)_3C\cdot$ by additional NOMP). These studies have helped delineate what activation temperatures favor certain kinds of sites.

3. Matrix Isolation of Single Metal Oxide Molecules

We are well equipped and experienced in the study of high temperature species such as free atoms and coordination deficient molecules.[30,31]. We are now initiating studies of single metal oxide molecules in low temperature matrices. This work is in the beginning stages and is intended to yield bench mark data as the ultimate model of the surface of metal oxides. Up to this point we have used laser, electron beam, and resistive heating methods to generate free molecules of TiO and VO since these are the most amenable to this approach. We have found that solid Ti_2O_3 and V_2O_3 are better sources of molecular TiO and VO than are solid TiO and VO. Reaction chemistry with Cl_2, 2,4-pentanedione, cyclopentadiene, and bipyridine have been investigated. One surprising result is the facile loss of oxygen as H_2O whenever mildly acidic hydrogens are available as a reaction partner. Matrix isolation spectroscopic studies are beginning.

4. Theoretical Approaches to Understanding MgO and CaO Isolated Molecules: Spectroscopic Properties and Coordination to CO.

One Ph.D. candidate working jointly with KJK and JOV is investigating MgO and CaO by theoretical methods. Matrix isolation experimental studies will be carried out in conjunction later.

Ab initio calculations on CO complexes with metal oxides have yielded several results that will motivate further experimentation. The standard program package[32] Gaussian 82 has been employed in these studies. Additional codes for performing SCF calculations with effective core poentails[33] have also been employed when the metal atom belongs to the fourth period. Geometries can be fully optimized, with gradients of the total energy evaluated analytically.

The first target of this study was complex formation between MgO and CO. Weak van der Waals binding occurs when the CO attacks at the O of MgO, regardless of whether the C or the O of CO is pointed at MgO. A stable complex is formed when the CO donates an electron pair to the Mg. The electronic structure is roughly that of a Mg^{2+} ion with a CO and oxide ligands. No back donation into the π* of the CO occurs, as Mg^{2+} has no valence electrons. It is possible to optimize another stable geometry in which the CO is bound to the metal through the oxygen atom. Both structures are approximately linear. These two geometries are optimized at the SCF double τ plus polarization level; correlation corrections at these geometries are estimated with second order perturbation theory. Vibrational frequencies are also calculated in the even that experimental spectra can be observed.

When the metal is changed to Ca, several differences from the Mg results become prominent. Upon choosing reasonable values for bond distances in an approximately linear geometry, the carbonyl and isocarbonyl structures spontaneously convert to highly bent structures. The latter guess geometry connects smoothly to a planar, four-member ring with the C and Ca^{2+} atoms opposite each other. The electronic structure is approximately a Ca^{2+} ion with a CO_2^{2-} chelating ligand. In this C_{2v} structure, the anion is isoelectronic with CF_2. The HOMO of the free anion donates in a σ fashion to the empty s, $\vec{p}$ and d orbitals of the cation. Upon assuming the former initial guess geometry, a smooth conversion to another ring-containing structure occurs. A three-member ring with Ca, O and C forms. One can understand this species as a complex of the same anion and cation as before, but with the latter bridging between the C and one of the O atoms. These Ca results suggest that similar ring structures may exist for the Mg case. A four-member ring structure with Mg has been found, but no stable three-member ring was obtained.

Further work on complexes with early transition metals is now in progress to examine the effects of d electrons on the bonding. The alternatives of simple CO binding or formation of CO_2^{2-} suggest that subtle differences in metal atom size and electronegativity may have great consequences for catalytic reactivity on metal oxide surfaces.

REFERENCES

1. Tanabe, K.; "Solid Acids and Bases," Academic Press, New York and Kodansha, Tokyo, 1970.

2. Henderson, B.; Wertz, J. E.; Adv. Phys., 70, 749, (1968); Taylor, E. H.; Adv. Catal., 18, 111, (1968); Henderson, B.; Wertz, J.E., "Defects in the Alkaline Earth Oxides," Halsted Press, New York, (1977).

3. W. Van Gool, "Principles of Defect Chemistry of Crystalline Solids," Academic Press, New York (1966), p. 14.

4. Japanese scientific teams at Hokkaido University (Tanabe, Hattori), U. of Tokyo (Yoneda), Kyushu Univ. (Mochida), Tokyo Inst. (Akai) and others are heavily involved. French teams at U. of Paris (Che) and CNRS-Lyon (Teichner) are also active. However, each group has its own interest and special direction.

5. M. Che and G.C. Bond, editors, "Adsorption and Catalysis on Oxide Surfaces," Studies in Surface Science and Catalysis 21, Elsevier Pubs., Amsterdam (1985).

6. A.R. West, "Solid State Chemistry and Its Applications," Wiley, New York, 1984.

7. a.) E. Sondor and W.A. Sibley, "Point Defects in Solids." J.H. Crawford, and L.M. Slifken, eds., Plenum, New York, 1972. b) A.L.G. Rees, "Chemistry of the Defect Solid State," Muthuen, Landon and Wiley, New York, 1954.

8. G. Lempfuhl and Y. Uchida, Ultramicroscopy, 4, 275 (1979).

9. a) W. Schottky, Z. Physik, Chem., B29, 335, (1935);   b) W. Schottky, Naturwissenschaften, 23, 656 (1935); c) A.E. Hughes and B. Henderson, "Defects in Crystalline Solids," J. H. Crawford and L.M. Slifkin, eds., Plenum, New York, 1972.

10. a) E.H. Taylor, Adv. Catal. Relat. Sub.., 18, 111 (1968); b) M.M. Abraham, Y. Chen., L.A. Boatner, and R.W. Reynolds, Sol. Stat Comm., 16, 209 (1975)

11. Klabunde, K.J.; Kaba, R.; Morris, R.; "Inorganic Compounds with Unusual Properties--II," Advances in Chemistry Series, No. 173, American Chem. Soc., 1979, paper 13, page 140.

12. T. Ushikwbo, H. Hattori, and K. Tanabe, Chemistry Letters (Japan), 649 (1984).

13. K. Tanabe, A. Kayo, and T. Yamaguchi, J. Chem. Soc., Chem. Comm., 602 (1981).

14. M. Hiro and K. Arata, J. Chem. Soc., Chem. Comm, 112 (1985).

15. M. Utiyama, H. Hattori, and K. Tanabe, J. Catal., 53, 237 (1978).

16. M. F. Hoq and K. J. Klabunde, J. Am. Chem. Soc., 108, 2114 (1986).

17. M. F. Hoq and K. J. Klabunde, Unpublished results (in preparation)

18. J. E. Garrone and F. S. Stone, Proc. 8th Int. Cong. Catal., III, Verlag Chemie, 441 (1984).

19. M. Boudart, A. Delbouille, E.G. Derouane, V. Indovina, and A.B. Walters, J. Am. Chem. Soc., 94, 6622 (1972).

20. H. Hattori, Y. Tanaka, and K. Tanabe, J. Am. Chem. Soc., 98, 4652 (1976).

21. a) D.J. Driscoll, W. Martir, J.X. Wang and J.H. Lunsford, J. Am. Chem. Soc., 107, 58 (1985);   b) T. Ito, J.X. Wang, C.H. Lin and J.H. Lunsford, J. Am. Chem. Soc., 107, 5062 (1985).

22. K. J. Klabunde and H. Matsuhashi, J. Am. Chem. Soc., 109, 1111 (1987).

23. a) A. J. Tench and R. L. Nelson, Trans. Faraday Soc., 63, 2254 (1967); b) S. Coluccia, A. Chiorino, F. Gugglielminotti, and C. Morterra, J. Chem. Soc. Faraday Trans., 1, 75, 2188 (1979);   c) T. Iizuka, Chem. Lett. 891 (1973);   d) H.S.W. Massey, "Negative Ions," University Press, Cambridge, 1950;   e) E.R.S. Winters, Adv. Catal., 10, 196 (1958).

24. R.M. Morris and K.J. Klabunde, J. Am. Chem. Soc., 105, 2633 (1983) and references therein.

25. F. Mousa and K.J. Klabunde, Synthesis, submitted.

26. S. T. Lin and K. J. Klabunde, Langmuir, 1, 600 (1985).

27. a) C. A. Evans, _Aldrichimica. Acta_, 12, 23 (1979);
    b) V. P. Oleshko, T. V. Bychkova, V. B. Golubev, E. V. Lunina, and L. I. McKarosov, _Russian J. Phys. Chem._, 52, 605 (1978).

28. I. Nieves and K. J. Klabunde, "Materials Chemistry and Physics," K. Tanabe, editor, Elsevier, in press.

29. I. Nieves and K. J. Klabunde, in preparation.

30. K. J. Klabunde, "Chemistry of Free Atoms and Particles", Academic Press, New York (1980).

31. K. J. Klabunde, editor, "Thir Films from Free Atoms and Particles," Academic Press, Orlando (1985).

32. Gaussian 82, Release A by J. S. Binkley, D. DeFrees, M. Frisch, E. Fluder, J. A. Pople, K. Ragavachari, H. B. Schlegel, R. Seeger and R. Whiteside, Carnegie-Mellon University, Pittsburgh, PA.

33. P. J. Hay and W. R. Wadt, _J. Chem. Phys._, 82, 299 (1985).

34. An example is the 6-31G basis. W. J. Hehre, R. Ditchfield and J. A. Pople, _J. Chem. Phys._ 56, 2257 (1972); P. C. Kariharan and J. A. Pople, _Theoret. Chim. Acta_ 28, 213 (1973).

35. M. J. Frisch, J. A. Pople and J. S. Binkley, _J. Chem. Phys._, 80, 3265 (1984); T. Clark, J. Chandrasekhar, G. W. Spitznagel and R. V. R. Schleyer, _J. Comput. Chem._ 4, 294 (1983).

36. R. Bartlett, _Ann. Rev. Phys. Chem._ 32, 359 (1981); J. S. Binkley and J. A. Pople, _Int. J. Quant. Chem._ 9, 229 (1975).

37. P. J. Hay and W. R. Wadt, _J. Chem. Phys._ 82, 299 (1985).

38. J. V. Ortiz, R. Basu and Y. Ohrn, _Chem. Phys. Lett._ 103, 29 (1983).

39. K. J. Klabunde and A. Whetten, _J. Am. Chem. Soc._, 108, 6529 (1986).

40. G. H. Jeong and K. J. Klabunde, _J. Am. Chem. Soc._, 108, 7103 (1986).

41. G. H. Jeong, Ph.D. Thesis, Kansas State University (1987).

42. G. Cardenas-Trivino, P. Shevlin, and K. J. Klabunde, _Inorg. Chemica Acta._, in press.

Publications resulting from ARO Grant

43. S. T. Lin and K. J. Klabunde, "Thermally Activated Magnesium Oxide Surface Chemistry. Adsorption and Decomposition of Phosphorus Compounds." _Langmuir_, 1985, 1, 600-605.

44. M. F. Hoq and K. J. Klabunde, "Thermally Activated Magnesium Oxide as a Selective Deuteration Catalyst Under Mild Conditions," _J. Am. Chem. Soc._, 1986, 108, 2114-2116.

45. K. J. Klabunde and H. Matsuhashi, "A Comparison of Electron Donor and Proton Abstraction Activities of Thermally Activated Pure Magnesium Oxide and Doped Magnesium Oxides," <u>J. Am. Chem. Soc.</u> <u>1987</u>, <u>109</u>, 1111-114.

46. K. J. Klabunde, M. F. Hoq, F. Mousa, and H. Matsuhashi, "Metal Oxides and their Physico-Chemical Properties in Catalysis and Synthesis," invited book chapter for <u>Preparative Chemistry Using Supported Reagents</u>, P. Laszlo, editor, Academic Press, in press.

47. J. M. White, J. E. Kerdt, K. Klabunde, J. Shapley, and J. Yates, "Catalytic and Stoichiometric Destruction of Organic Heteratom Compounds," Palintir Study Group Report, U.S. Army Research Office, November <u>1986</u>. A review in <u>J. Phys. Chem.</u> entitled "The Surface Chemistry of Organo-Phosphorus Compounds" is submitted.

48. I. Nieves and K. J. Klabunde, "Nature of Chemisorbed Species on Metal Oxide Surfaces. Electron Transfer and Bond Breaking Processes," invited book chapter for <u>Advances in Basic Solid Materials-Materials Chemistry and Physics</u>, K. Tanabe, editor, Elsevier, in press.

40. F. Mousa and K. J. Klabunde, "Base Condensation of Carbonyl Compounds on Thermally Activated Magnesium Oxide," <u>Synthesis</u>, submitted.

Three other papers in are in preparation.

Scientific Personnel

M. F. Hoq, Ph.D. expected in August 1987

S. Utamapanya, Ph.D. expected in December 1988.

I. Nieves, visiting professor from U. of Puerto Rico

H. Matsuhashi, postdoctoral research associate

F. Mousa, postdoctoral research associate

T. Groshens, Ph.D. expected May 1988

END

11-87

DTIC